Structure Factor in the Presence of Shear - an RPA Calculation

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We consider the structure factor of a system of colloidal particles immersed in a host liquid. Each particle is assumed to be affected by forces due to other particles, a drag force proportional to the velocity of the particle relative to the local velocity of the fluid and a fluctuating random noise. The effect of the particles on the velocity field of the host liquid is neglected. The problem is treated within the RPA approximation which is a widely used tool in many body theory. The validity of the RPA result is discussed.

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We consider a system of identical particles immersed in a host liquid subject to an external linear shear flow. Such systems have beed studied experimentally and numerically for the last two decades [1] - [7]. The results of those studies showed not only distortion of the structure factor due to the external shear, but also more dramatic effects like shear induced ordering and jamming. The theoretical explanations were first given in a paper by S. Hess [8], followed by a number of other papers that tackled the problem from different angles [9] - [18]. It seems, however, that in spite of substantial advances made over the years, a simple and full theoretical description is still lacking. In the present paper we will obtain the shear dependent structure factor using an RPA approximation employed on an extension of the exact collective coordinates Fokker-Planck equation derived recently by Edwards and Schwartz [19]. The whole method is based on borrowing approximations that proved simple and effective in the study of quantum mechanical many body systems. Such methods have been applied in the past [20], [21] and much more simply recently [22] to obtain the Percus-Yevick (PY) [23] equation for a classical hard sphere system. We hope to produce the analog of the hard sphere PY equation for the case of shear flow in the very near future.

Our starting point is an assumption concerning the forces acting on each particle. We assume that each particle is affected due to forces applied by the other particles, by a drag force proportional to its velocity relative to the local velocity of the liquid and by a fluctuating noise which is assumed to be uncorrelated for different particles. It is further assumed that the velocity field of the liquid is given externally and is unaffected by the motion of the particles. This assumption will be checked in a future publictaion. We can say at present, that the main effect we expect from the inclusion of the modification of the velocity field by the system of particles is a modification of the interaction between particles and a modification of the noise. In any case, our present model is described by the set of Langevin equations

$$\gamma[\dot{\vec{r}}_i - \vec{V}(\vec{r}_i)] = -\nabla_i \sum_{j=1}^{N} w(\vec{r}_i - \vec{r}_j) + \vec{\eta}_i(t), \tag{1}$$

where $\vec{r}_i$ is the radius vector of the i'th particle, $\vec{V}(\vec{r})$ is the divergenceless velocity field of the liquid, γ is the friction constant, N is the number of particles, w is the two body potential between particles and $\vec{\eta}_i(t)$ is a random force acting on the i'th particle obeying

$$\langle \eta_i^k(t) \rangle = 0 \tag{2}$$

and

$$\langle \eta_i^k(t)\eta_j^l(t') \rangle = 2\sigma\delta_{ij}\delta_{kl}\delta(t-t'), \tag{3}$$

where k and l denote cartesian components of a vector. The Langevin equation above leads in a standard way to a Fokker-Planck equation for the probability distribution of particle coordinates, P

$$\frac{\partial P}{\partial t} = \frac{1}{\gamma}\sum_{i,k}\frac{\partial}{\partial r_{ik}}\left[kT\frac{\partial P}{\partial r_{ik}} + \frac{\partial U}{\partial r_{ik}}P - \gamma V_k(\vec{r}_i)P\right] \equiv LP, \tag{4}$$

where

$$U \equiv \frac{1}{2}\sum_{i\neq j} w(|\vec{r}_i - \vec{r}_j|)$$

is the total potential energy, and $kT \equiv \frac{\sigma}{\gamma}$. Since the particles are identical, the only relevant physical observables are functionals of the density

$$\rho(\vec{r}) \equiv \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i). \tag{5}$$

To be specific, we assume that our N particles are enclosed in a cubic box of volume V with periodic boundary conditions. The natural collective coordinates are the Fourier transforms of the density

$$\rho_{\vec{q}}(\{\vec{r_i}\}) \equiv N^{-\frac{1}{2}} \int \rho(\vec{r}) e^{-i\vec{q}.\vec{r}} d^3r \quad \text{for } \vec{q} \neq 0 \text{ with } q_i \equiv \frac{2\pi n_i}{V^{\frac{1}{3}}}. \tag{6}$$

The Fokker-Planck equation for the probability distribution of particle coordinates can be transformed into a Fokker-Planck equation for the probability distribution of collective coordinates by following the procedure outlined by Edwards and Schwartz [19]. We note first, that the probability distribution of the collective coordinates, $\widehat{P}(\{\rho_{\vec{q}}\})$, is given by

$$\widehat{P}(\{\rho_{\vec{q}}\}) \equiv \int P(\{\vec{r_i}\}) \prod_{\vec{q}\neq 0} \delta\left(\rho_{\vec{q}} - N^{-\frac{1}{2}} \sum_{j=1}^{N} e^{-i\vec{q}.\vec{r}_j}\right) \prod_{l=1}^{N} d^3r_l. \tag{7}$$

Therefore if $O(\{\vec{r_i}\})$ is an observable that can be written as $O(\{\rho_{\vec{q}}(\{\vec{r_i}\})\})$, then its thermodynamic average can be calculated by

$$\langle O \rangle = \int O(\{\rho_{\vec{q}}\}) \widehat{P}(\{\rho_{\vec{q}}\}) \prod_{\vec{q}\neq 0} d\rho_{\vec{q}}. \tag{8}$$

(A similar transformation was used previously for the case of equilibrium statistical physics [22]). We now obtain the Fokker-Planck equation for $\widehat{P}(\{\rho_{\vec{q}}\})$ by multiplying eq. (4) by

$$\prod_{\vec{q}\neq 0} \delta\left(\rho_{\vec{q}} - N^{-\frac{1}{2}} \sum_{j=1}^{N} e^{-i\vec{q}.\vec{r}_j}\right),$$

and integrating over the particle coordinates. In ref. [19] that considered a system without shear, an explicit equation is obtained for $\widehat{P}(\{\rho_{\vec{q}}\})$. Therefore, here we need only to introduce the term corresponding to the shear. Since the Fokker-Planck equation is linear, the form we obtain is

$$\frac{\partial \widehat{P}}{\partial t} = L_0 \widehat{P} + iN^{-\frac{1}{2}} \sum_{\vec{q},i,k} q_k \frac{\partial}{\partial \rho_{\vec{q}}} \left[\int e^{-i\vec{q}.\vec{r}_i} V_k(\vec{r_i}) P(\{\vec{r}_m\}) \prod_{\vec{p}\neq 0} \delta\left(\rho_{\vec{p}} - N^{-\frac{1}{2}} \sum_{j=1}^{N} e^{-i\vec{p}.\vec{r}_j}\right) \prod_{l=1}^{N} d^3r_l\right], \tag{9}$$

where L_0 is the linear operator obtained by Edwards and Schwartz [19]. We do not dwell here on bringing the term due to the shear for a general divergenceless velocity field to the form $\Delta L \widehat{P}$. We consider instead the special case of linear shear

$$\vec{V}(\vec{r}) = Cx\hat{z}. \tag{10}$$

In that case, the last term on the R.H.S of eq. (9) becomes

$$-C \sum_{\vec{q}} q_3 \frac{\partial \rho_{\vec{q}}}{\partial q_1} \frac{\partial \widehat{P}}{\partial \rho_{\vec{q}}}. \tag{11}$$

The full form of eq. (9), including the specific L_0 is thus given by

$$\frac{\partial \widehat{P}}{\partial t} = \frac{kT}{\gamma} \sum_{\vec{q}} \left\{ q^2 \left[\widehat{P} + \rho_{\vec{q}} \frac{\partial \widehat{P}}{\partial \rho_{\vec{q}}} + \frac{\bar{\rho}}{kT} w(\vec{q}) \widehat{P}\right] - \nu q_3 \frac{\partial \rho_{\vec{q}}}{\partial q_1} \frac{\partial \widehat{P}}{\partial \rho_{\vec{q}}} + N^{-\frac{1}{2}} \sum_{\vec{p}} \vec{q}.\vec{p} \left[-\rho_{\vec{q}+\vec{p}} \frac{\partial^2 \widehat{P}}{\partial \rho_{\vec{q}} \partial \rho_{\vec{p}}} + \frac{\bar{\rho}}{kT} w(\vec{p}) \rho_{\vec{q}-\vec{p}} \rho_{\vec{p}} \frac{\partial \widehat{P}}{\partial \rho_{\vec{q}}}\right] \right\}, \tag{12}$$

where $\nu \equiv \frac{\gamma C}{kT}$ and $w(\vec{q})$ is the Fourier transform of the inter-particle potential defined by

$$w(\vec{q}) \equiv \int w(\vec{r}) e^{-i\vec{q}.\vec{r}} d^3 r. \tag{13}$$

We will look for a stationary state of the system, hence the L.H.S vanishes. In order to keep the discussion simple, we will employ the RPA approximation on the R.H.S of eq. (12) by discarding all the third order terms except for those where one of the ρ's is $\rho_0 = \sqrt{N}$. (Note that derivatives with respect to ρ_0 do not appear). Thus, we're left with the following equation for the stationary probability distribution:

$$\sum_{\vec{q}} \left\{ q^2 \left[A^{-1}(\vec{q})\widehat{P} + A^{-1}(\vec{q})\rho_{\vec{q}} \frac{\partial \widehat{P}}{\partial \rho_{\vec{q}}} + \frac{\partial^2 \widehat{P}}{\partial \rho_{\vec{q}} \partial \rho_{-\vec{q}}} \right] - \nu q_3 \frac{\partial \rho_{\vec{q}}}{\partial q_1} \frac{\partial \widehat{P}}{\partial \rho_{\vec{q}}} \right\} = 0, \tag{14}$$

where $A^{-1}(\vec{q}) \equiv 1 + \frac{\bar{\rho}}{kT} w(\vec{q})$. We try a solution of eq. (14) of the form

$$\widehat{P}(\{\rho_{\vec{q}}\}) \equiv e^{-\frac{1}{2}\sum_{\vec{q}\neq 0} S^{-1}(\vec{q})\rho_{\vec{q}}\rho_{-\vec{q}}}. \tag{15}$$

(We denote the pre factor of $\rho_{\vec{q}}\rho_{-\vec{q}}$ in the above Gaussian form by $S^{-1}(\vec{q})$ since if such a form does realy solve eq. (14) then that pre factor will be, as follows from eq. (8), the inverse of the structure factor we are looking for.) The combination of equations (15) and (14) yields the following equation for the structure factor:

$$\sum_{\vec{q}} \left\{ q^2 \left[A^{-1}(\vec{q}) - S^{-1}(\vec{q}) - A^{-1}(\vec{q}) S^{-1}(\vec{q}) \rho_{\vec{q}}\rho_{-\vec{q}} + S^{-2}(\vec{q})\rho_{\vec{q}}\rho_{-\vec{q}} \right] + \nu q_3 S^{-1}(\vec{q}) \frac{\partial \rho_{\vec{q}}}{\partial q_1} \rho_{-\vec{q}} \right\} = 0. \tag{16}$$

The last term in eq. (16) can be rewritten as

$$\sum_{\vec{q}} \nu q_3 S^{-1}(\vec{q}) \frac{\partial \rho_{\vec{q}}}{\partial q_1} \rho_{-\vec{q}} = \sum_{\vec{q}} \frac{\nu}{2} q_3 S^{-1}(\vec{q}) \frac{\partial}{\partial q_1} [\rho_{\vec{q}}\rho_{-\vec{q}}]. \tag{17}$$

Integrating eq. (17) by parts and combining the result with the rest of the terms in eq. (16) gives

$$\sum_{\vec{q}} \left\{ q^2 \left[A^{-1}(\vec{q}) - S^{-1}(\vec{q}) \right] + \left[-q^2 A^{-1}(\vec{q}) S^{-1}(\vec{q}) + q^2 S^{-2}(\vec{q}) + \frac{\nu}{2} q_3 S^{-2}(\vec{q}) \frac{\partial S(\vec{q})}{\partial q_1} \right] \rho_{\vec{q}}\rho_{-\vec{q}} \right\} = 0. \tag{18}$$

This equation for the static structure factor should hold for every collective coordinates configuration, $\{\rho_{\vec{q}}\}$, hence the following conditions must be obeyed:

$$\sum_{\vec{q}} q^2 \left[A^{-1}(\vec{q}) - S^{-1}(\vec{q}) \right] = 0 \tag{19}$$

and

$$1 - \frac{S(\vec{q})}{A(\vec{q})} + \frac{\nu}{2} \frac{q_3}{q^2} \frac{\partial S(\vec{q})}{\partial q_1} = 0. \tag{20}$$

Although it seems that the fact that there is a redundant condition here may cause trouble, it can be easily verified that any solution of the second condition also satisfies the first condition. Viewing the second condition as an ordinary differential equation in q_1 leads to a solution which depends on an initial condition. This condition is determined by applying the constraint that the structure factor must be finite for all the $\vec{q}'s$. The structure factor turns out to be

$$S(\vec{q}) = \frac{2}{\nu q_3} \int_{q_1}^{sign(\nu q_3)\cdot\infty} dq_1' q'^2 e^{-\frac{2}{\nu q_3}\int_{q_1}^{q_1'} dq_1'' \frac{q''^2}{A(q'')}}, \tag{21}$$

where $\vec{q}' \equiv (q_1', q_2, q_3)$ and $\vec{q}'' \equiv (q_1'', q_2, q_3)$. This is the RPA dependence of the structure factor on the shear rate. A number of points have to be addressed now. The structure factor is given here in terms of the Fourier transform of the inter-particle potential, $w(\vec{q})$. In the case when $w(\vec{q})$ does exist, one may replace $A^{-1}(\vec{q})$ in eq. (21) by the simplest RPA approximation for the structure factor in the absence of shear

$$S_0^{-1}(\vec{q}) = 1 + \frac{\bar{\rho}}{kT} w(\vec{q}). \tag{22}$$

Indeed, in the limit of zero shear rate, our calculation does yield the well known RPA result (22). However, The experience with non sheared liquids suggests that even when $w(\vec{q})$ exists, in most cases such RPA approximations produce bad results. A useful alternative is to turn eq. (22) around and to calculate an effective potential out of the externally given structure factor. This procedure actually replaces $w(\vec{r})$ by the Ornstein-Zernike direct correlation function. Rewriting eq. (21) using an externally given $S_0^{-1}(\vec{q})$ recovers exactly the expression given by Ronis [11] for the structure factor in the presence of shear. However, a further study of the Ronis expression reveals an interesting discrepancy when hard spheres interactions are considered. The structure factor in the absence of shear, $S_0(\vec{q})$, must have the property that the associated pair distribution function vanishes within the hard spere diameter. Further more, $S(\vec{q})$, the structure factor in the presence of shear, must also have this property. Unfortunately, it seems that this property does not follow from the Ronis expression when inesrting the external expression for $S_0(\vec{q})$ given by Wertheim [24] - Thiele [25] into the Ronis expression. We expect to deal with this problem in the very near future.

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